Simulation of a nano-particle in a dense polymer melt: role of interactions

Effect of a nanoscopic particle on melt structure and dynamics*

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*general applications to polymer-surface problems

Filled Polymers and Composites

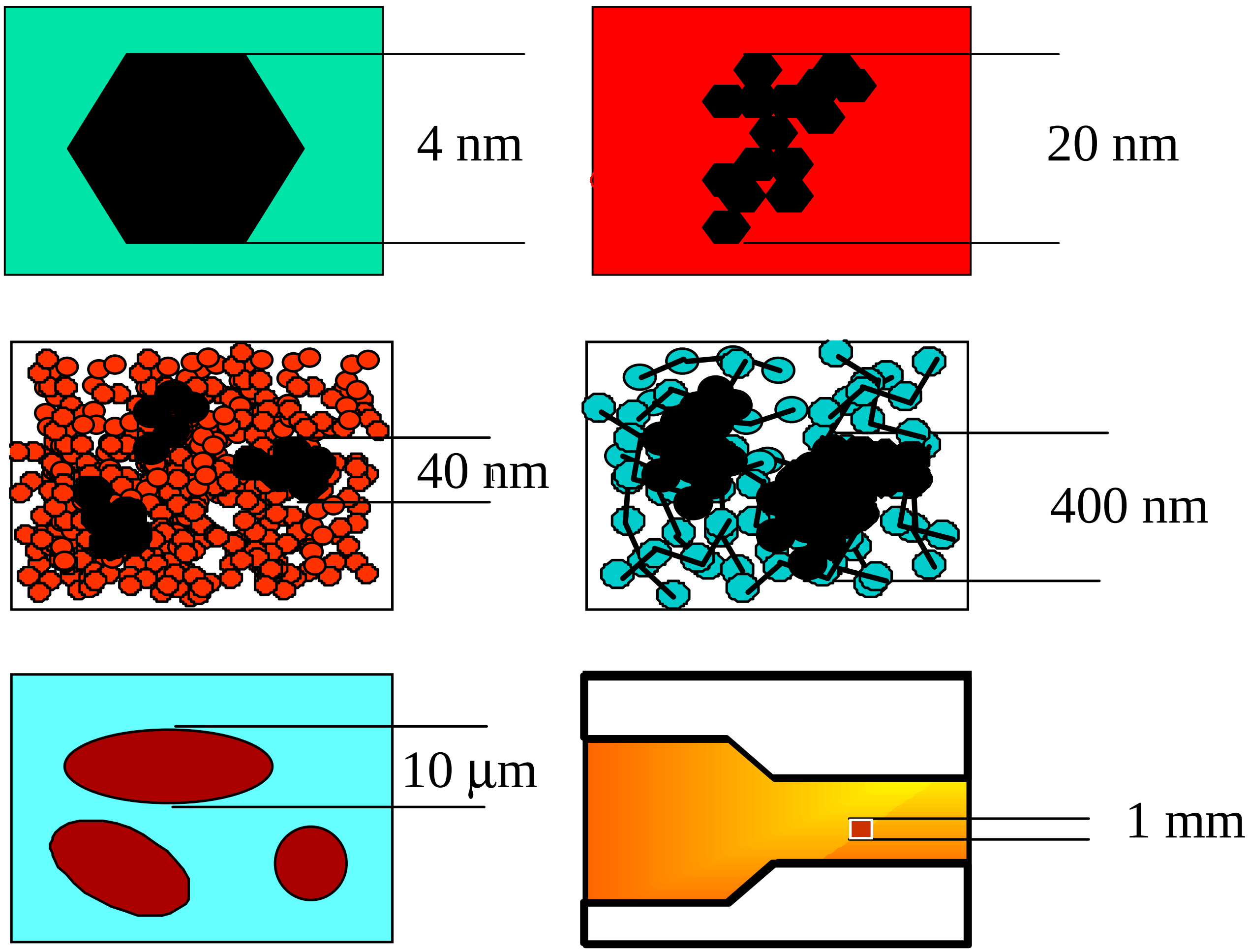
- Improve mechanical, rheological, dielectric, optical and other properties
- Low tech: tires, bumpers, paints and coatings
- High tech: micro- and nano-electronic devices
- Nanofillers
  - Tailor size and interactions to make specific property modifications
  - Improved dispersion – less material required

Goals of this work:

- Structure near the particle surface
- Shift of Glass Transition Temperature T_g
- Dynamics near the particle surface
- Role of a free surface

Multiple Length Scales in Filled Polymers

We focus on
smallest
length scales

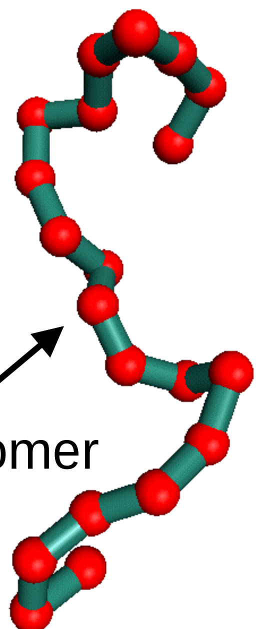


Simulation Model

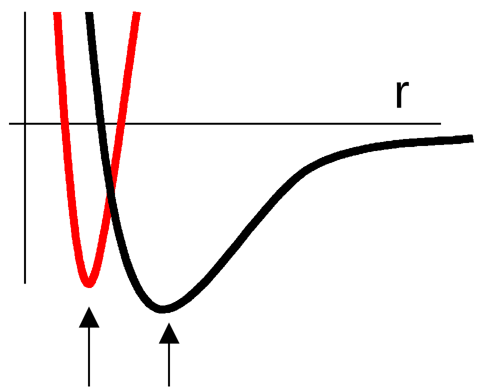
Bonded monomers or filler-sites

$$V_{\alpha\beta}(r) = -k/2\ R_o^2 \ln[1-(r/R_o)^2]$$

Polymer



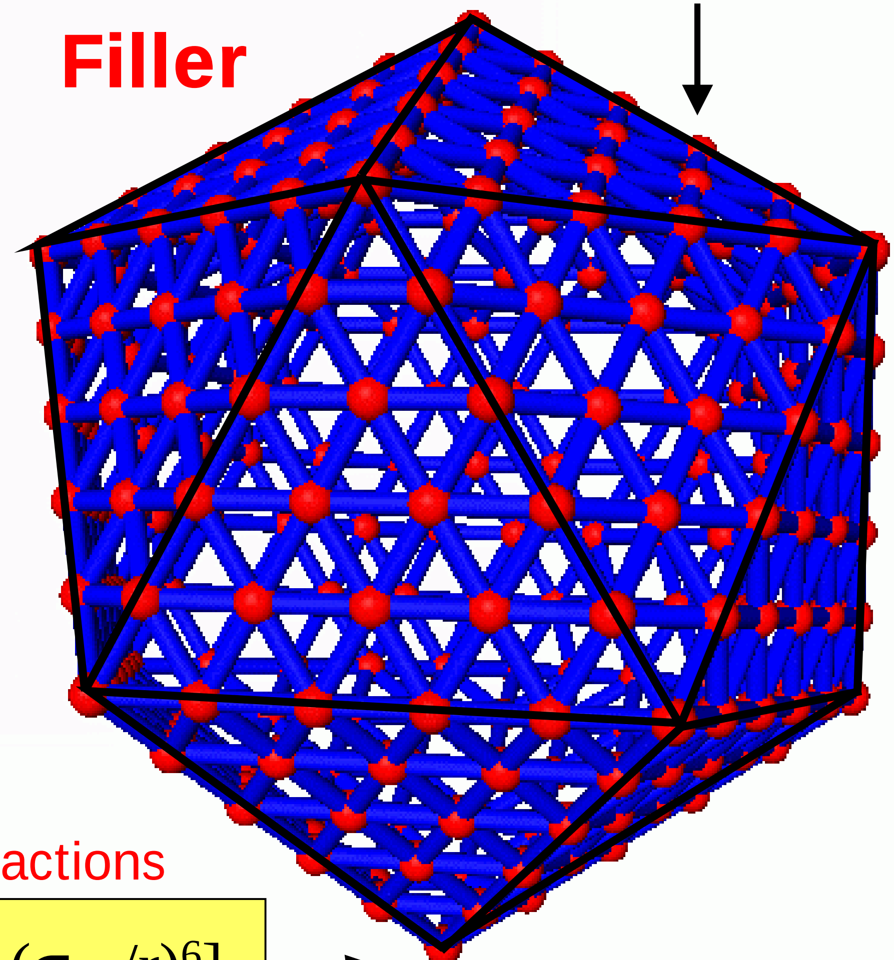
monomer



Mismatch inhibits crystallization

Filler

filler site



Monomer/filler-site interactions

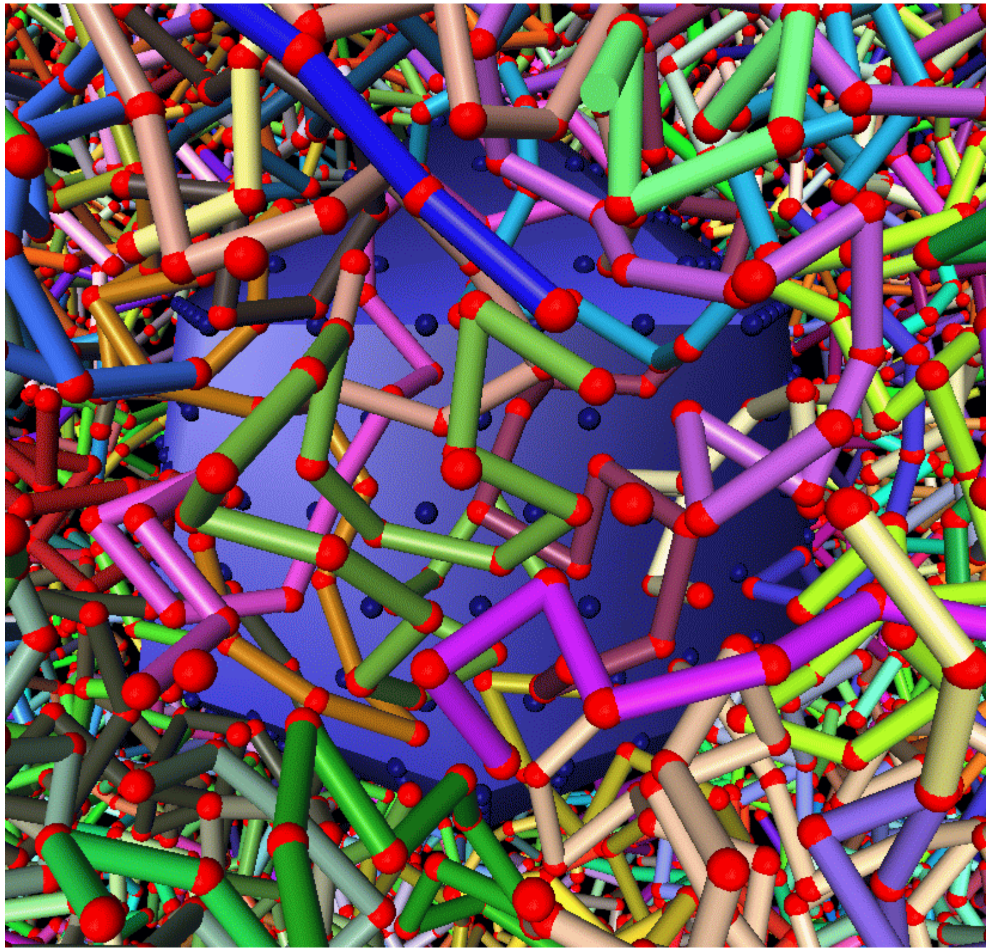
$$V_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$$

Leave off for excluded volume only

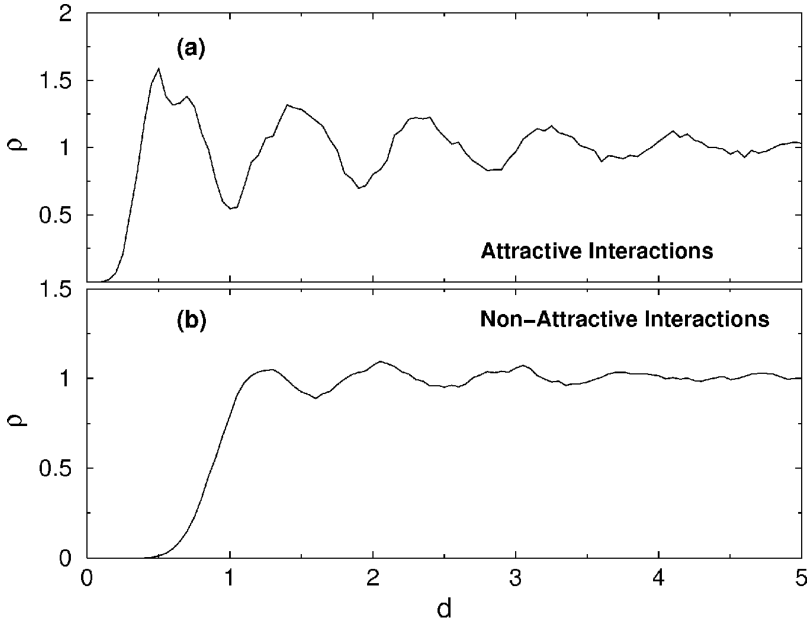
$\varepsilon_{mm} = 1.0$
$\varepsilon_{ss} = 2.0$
$\varepsilon_{ms} = (\varepsilon_{mm}\varepsilon_{ss})^{1/2}$

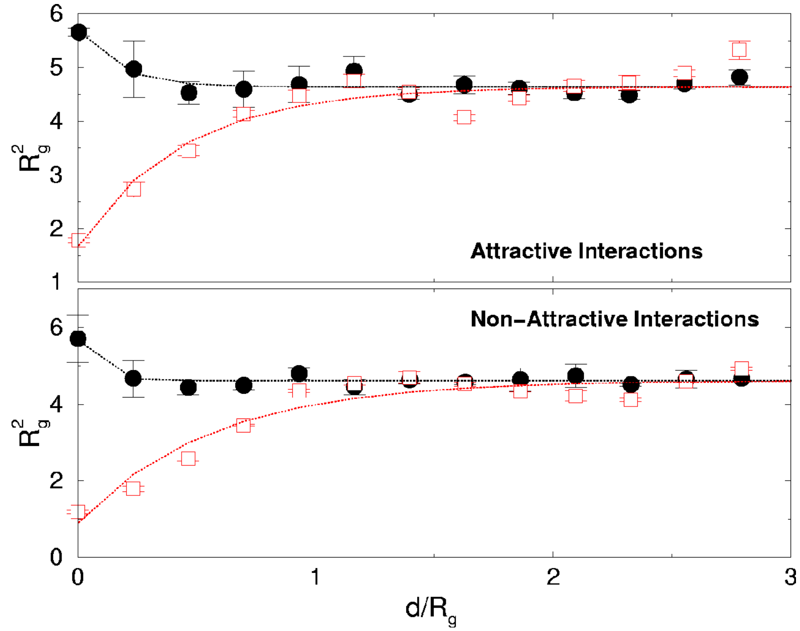
Simulation details

- 100 to 400 chains of 20 monomers each at melt density ρ=1.0
- Box size gives ρ_∞ within 0.2% of pure system density
- 0.35 < T < 2.0
- Simulation times up to ≈ 40 ns



Change of melt structure: density profile and chain conformation





Monomers form well-defined layers surrounding the particle

Layering occurs without attraction; location of first peak is *T* dependent

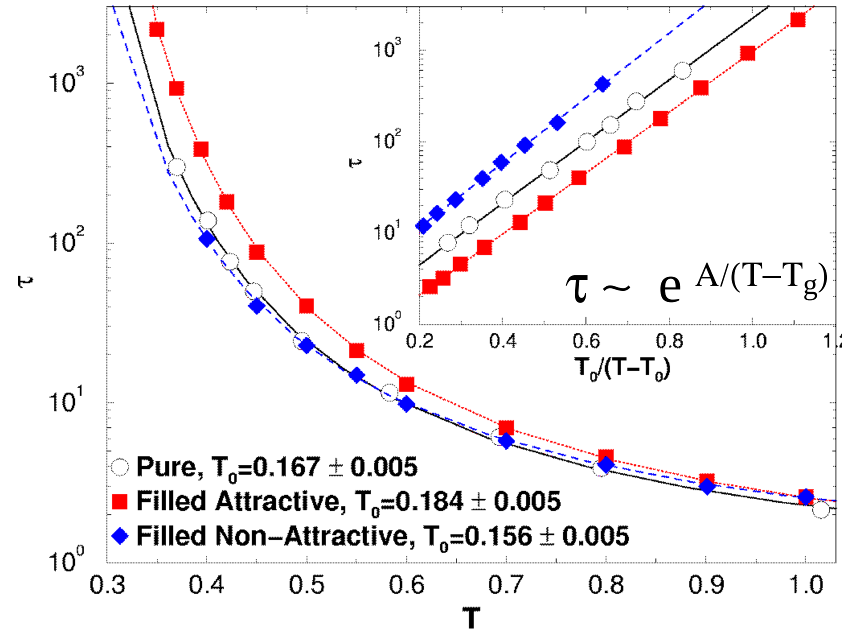
Chains orient with surface, regardless of type or strength of interaction.

Effect persists out to ~R_g

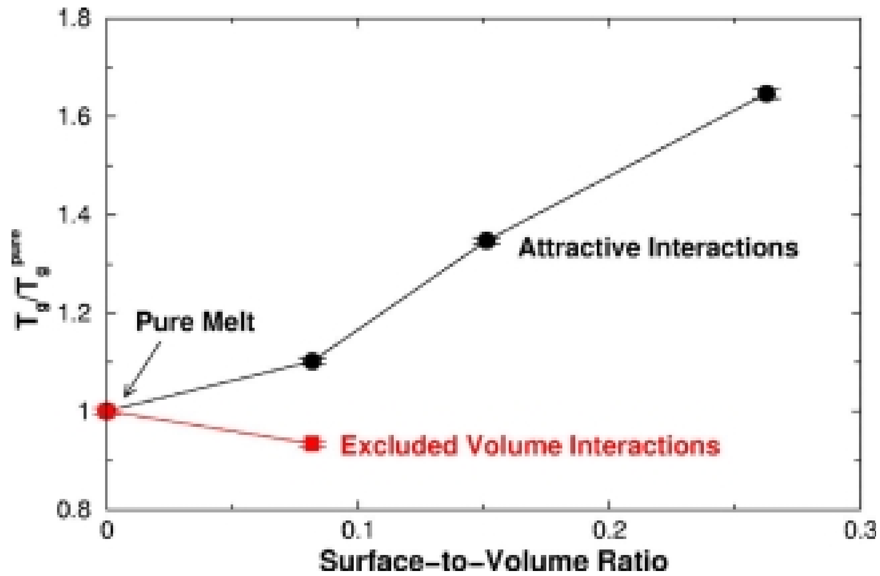
Results similar to ultra-thin films and simple surfaces, suggesting behavior is insensitive to moderate changes in surface geometry

Change of melt dynamics: T_g shift

- Glass transition shift depends on interactions
  - Attractive surface interactions slow dynamics, shift T_g up
  - Neutral or repulsive interactions enhance dynamics, shift T_g down

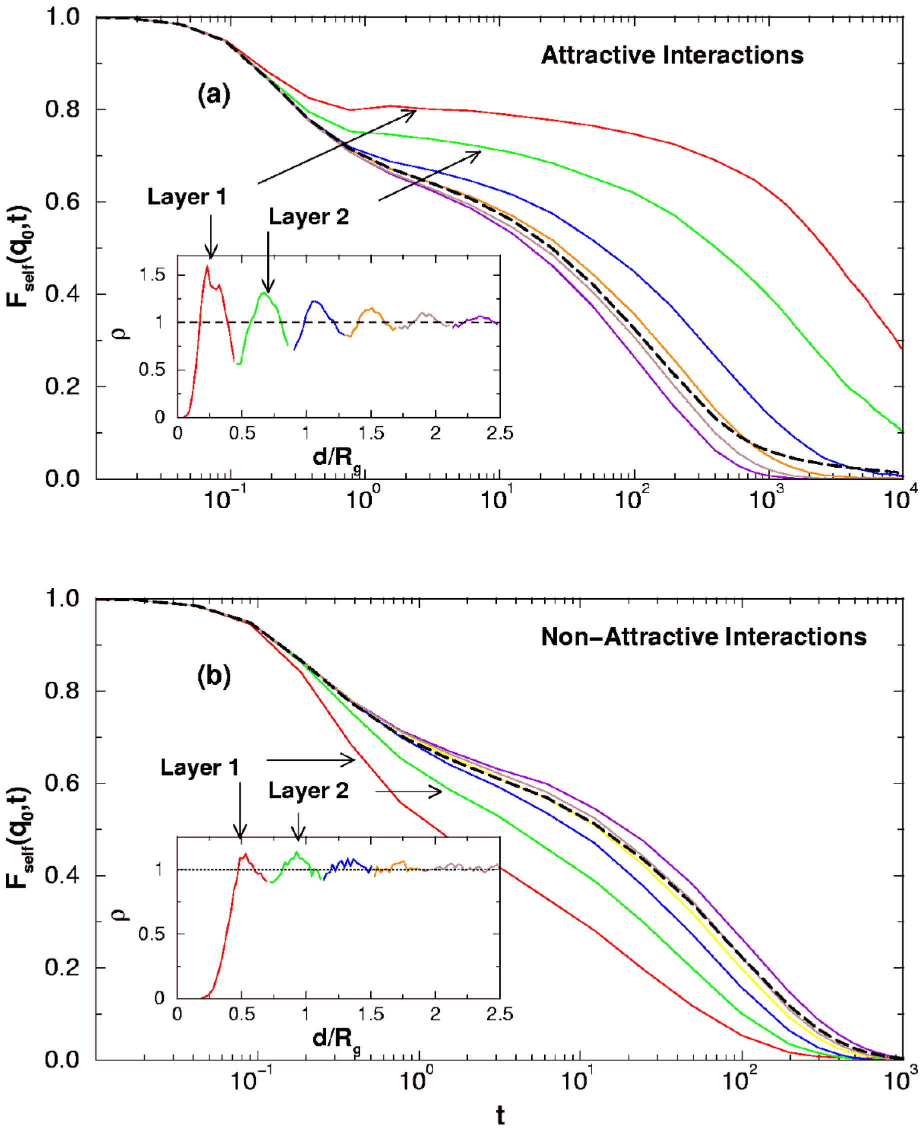


- Shift enhanced by increasing surface-to-volume ratio
  - Demonstrates importance of surface dynamics



Change of melt dynamics: Surface relaxation

- Attractive Interactions: surface dynamics are slowest
  – shift T_g up
- Non-Attractive Interactions: surface dynamics are fastest
  – shift T_g down
- Dynamics far from surface unchanged
  – Confinement important for lower T and/or longer chains –- in progress



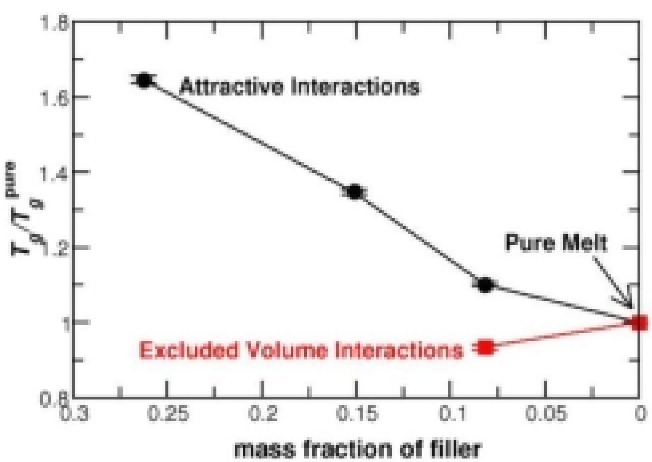
Nano-particle vs. Ultra-thin films

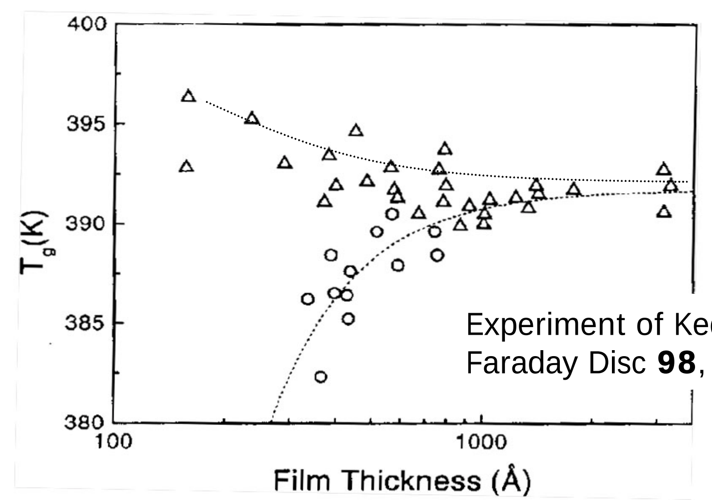
Nano-particle system

- Polymers are elongated and flattened near particle surface
- Strongly (weakly) attractive filler increases (decreases) T_g
- Strongly (weakly) attractive particle slows (speeds up) monomer dynamics.
- T_g shifts are more pronounced the higher the filler concentration

Ultra-thin films

- Polymers are elongated and flattened near substrate
- Strongly (weakly) attractive substrate increases (decreases) T_g
- Strongly (weakly) attractive substrate slows (speeds up) segmental dynamics.
- T_g shifts are more pronounced the thinner the film





Experiment of Keddie, et al.; Faraday Disc **98**, 219 (1994)

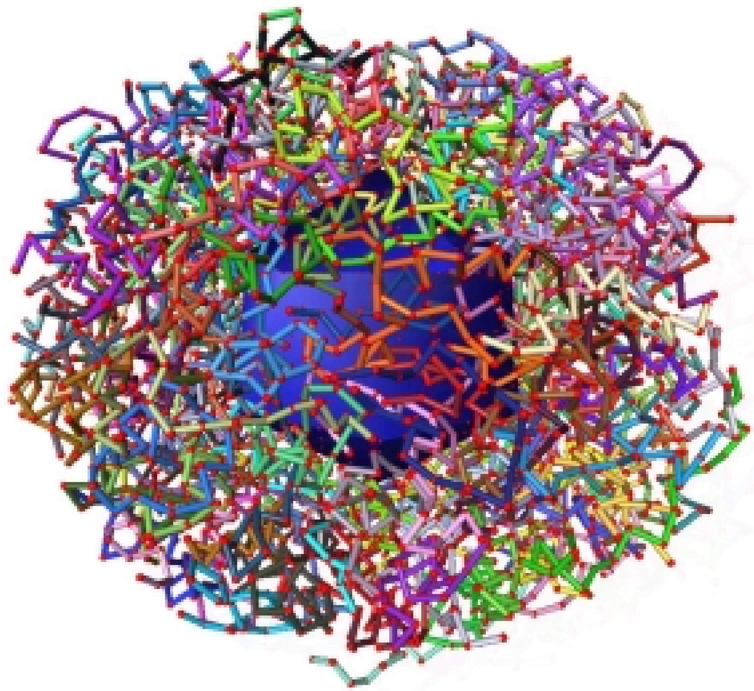
Filled polymers vs. ultra-thin films

- Our findings support that interactions play a key role in the observed changes in the dynamics and structure of polymers near surfaces
- Confinement should cause additional perturbation
- Filled melts and ultra-thin films may be interpreted within the same theoretical framework?

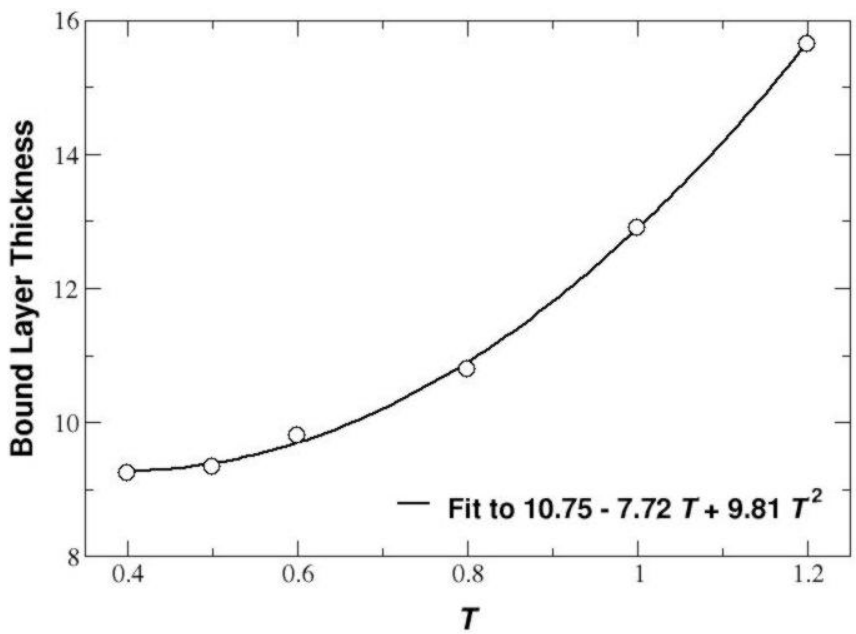
Effect of a free surface

Free surfaces occur in (e.g.):

- Extracted “bound polymer” of filled melts
- Free-standing films



Temperature dependent thickness

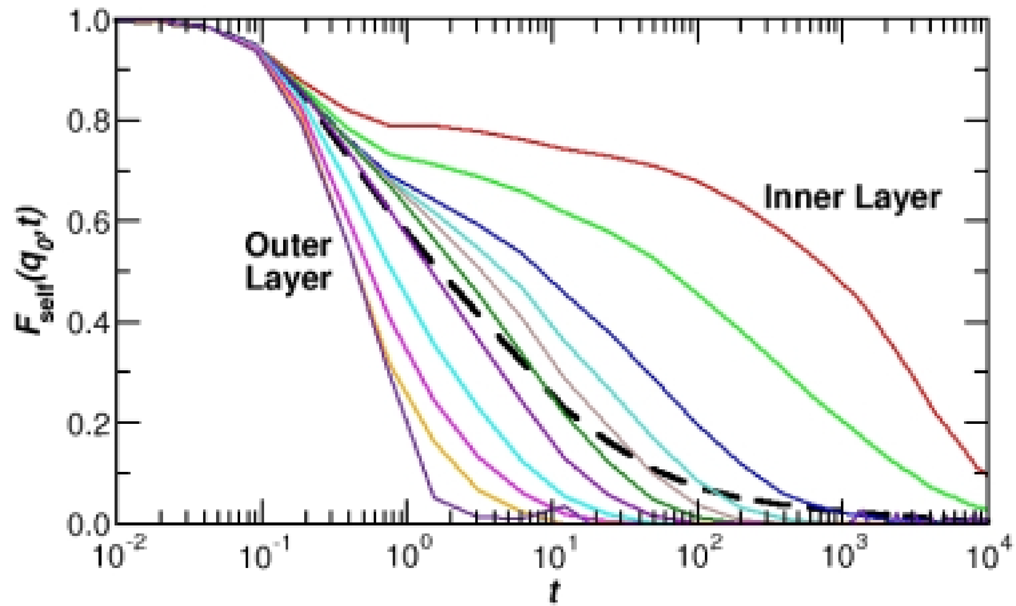


Thickness depends quadratically on temperature

Dynamics with a free surface

- Monomers near free surface are less constrained
- Significantly faster dynamics near the free surface

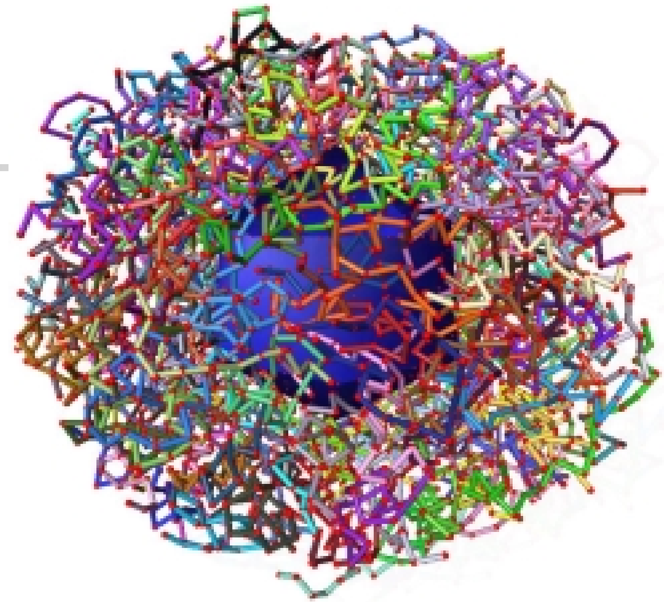
- Estimated $T_g < T_g^{pure}$!! Opposite expectations for attractive interactions

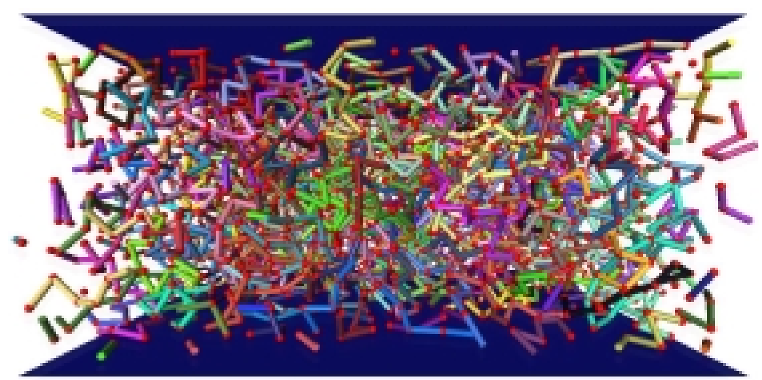


Prediction of bulk properties based on surface interactions complicated when melt is unconstrained at at least one surface

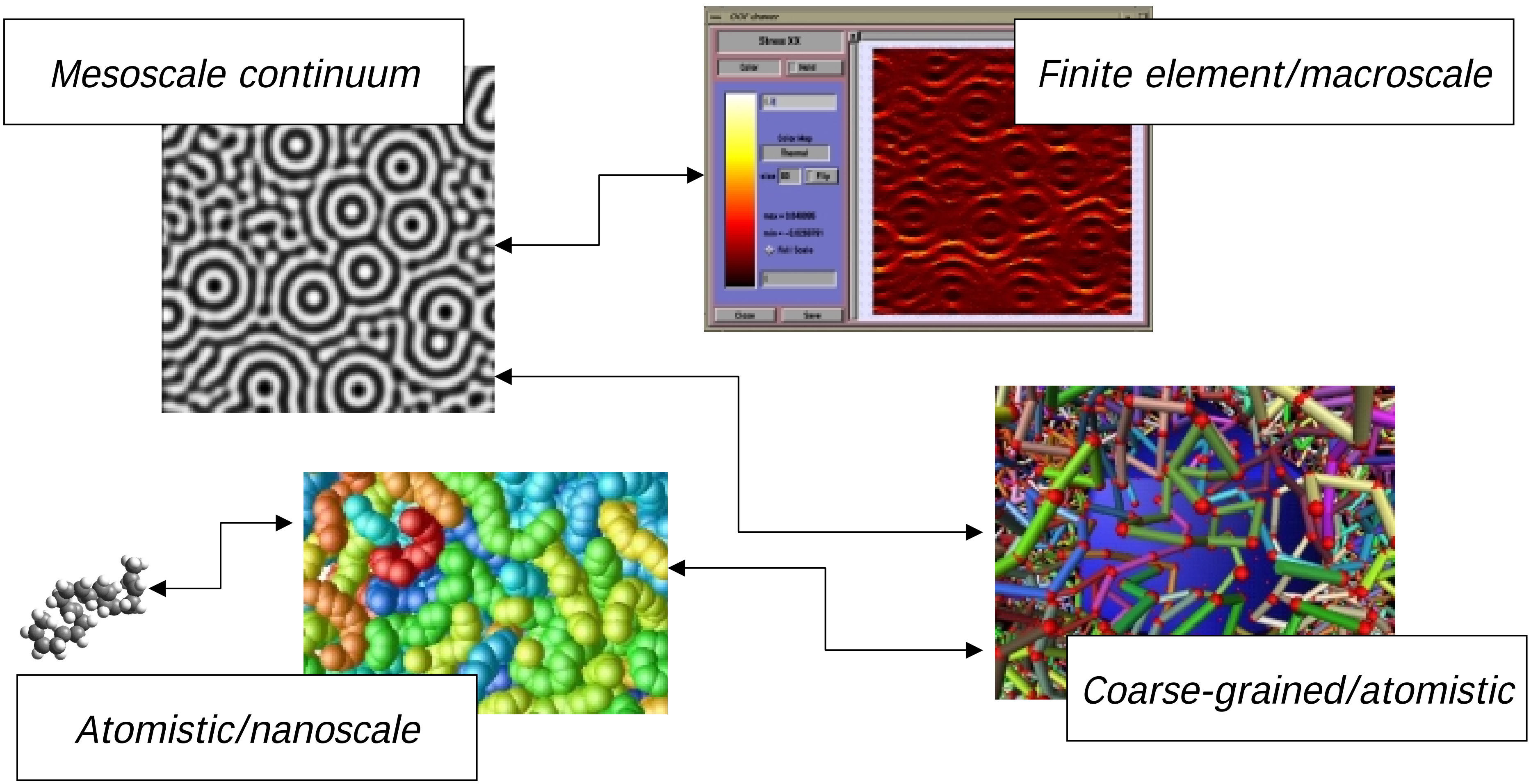
Summary

- Changes induced by nano-particle are general to "simple" surfaces
- T_g shifted in a predictable way by appropriate tuning the polymer-surface interactions
- A gradual change of the dynamics close (< $2R_g$) to the filler surface causes the change in T_g.
- Interpretation in the presence of a free surface complicated

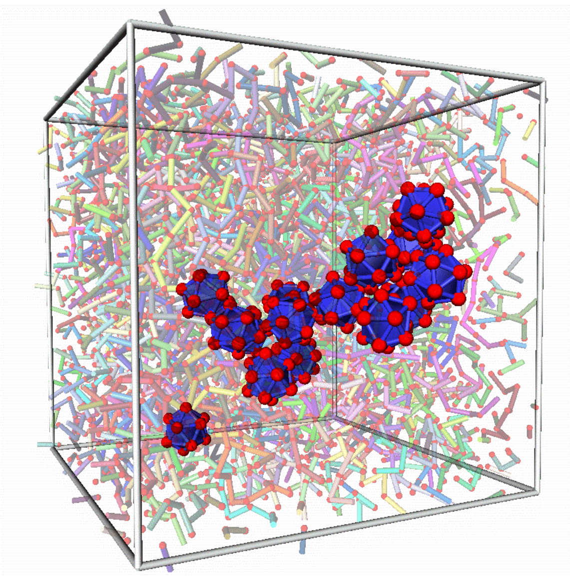




Multiscale simulation of filled and nano-filled polymers



Multiple Nano-fillers

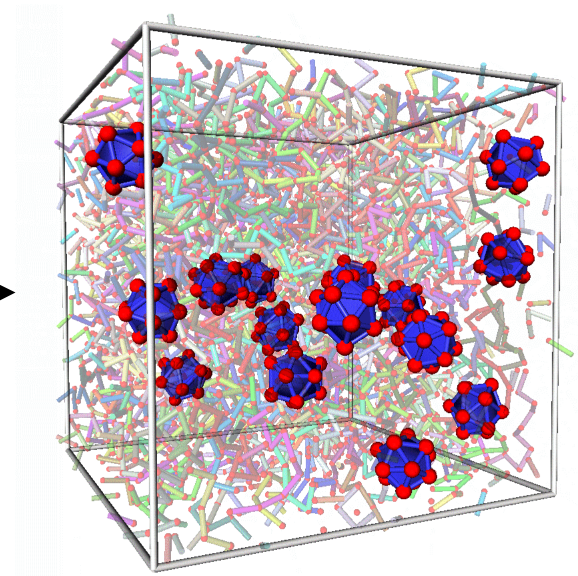


Factors controlling

Aggregation

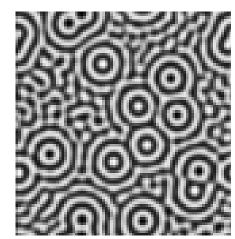
vs.

Dispersion



- Properties of dynamic clustering
- Change of morphology under shear

- Map to mesoscale



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